



A sustainable material for removal of heavy metals from water: adsorption of Cd(II), Pb(II), and Cu(II) using kinetic mechanism

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ABSTRACT

This study evaluated the potential of using avocado seed powder to remove the heavy metal ions in water as an adsorbent. The presence of permeable structure was identified using scanning electron microscopy and Fourier transform infrared analysis which is required for any material to remove heavy metal using adsorption technique. The effect of seed powder on pH, metal ion concentration, temperature, and contact time were assessed using the batch technique. The maximum adsorption was achieved at optimum conditions of 40 min to adsorb Cd²⁺, Cu²⁺, and Pb²⁺ heavy metals at an efficiency of 98.23%, 99.12%, and 99.29%, respectively. Meanwhile, the adsorption capacity of Cu²⁺, and Pb²⁺ were found to be 178.21 and 79.3 mg/g, respectively. However, the adsorption capacity of avocado seed fibers was less dependent on temperature. The voids in seed powder surface had been incredibly decreased after adsorption of metal ions which may have happened because of the bond arrangement with the groups present on the adsorbent. The avocado seed fibers act as a sustainable adsorbent material to remove heavy metal ions and the potential effects of the seed fibers had been explored in this study.

Keywords: Sustainable low-cost material; Avocado seed powder; Heavy metals; Adsorption capacity

1. Introduction

Heavy metals in water systems are non-biodegradable and cause the severe problem to the environment. Consumption of heavy metal contaminated water absorbed by the plant systems and transferred to the next level of the food chain with higher concentration is referred to as biomagnifications [1,2]. Water pollution has become a serious threat to human beings, plants, and animals. The effluents coming out from the water treatment plants contain enormous amounts of heavy metals which include copper, lead, zinc, and cadmium. The removal of such metals is of greater significance in water pollution control [3]. The consumption of water that contains lead causes adverse

effects on the organs of the human body includes kidneys, brain and bones, the textile industries, paint, metal finishing, and pigment industries are the major contributors of lead and cadmium in water [4].

Due to the rapid rise in population, the need for freshwater for several uses would increase. The demand for freshwater would rise rapidly and the gross per capita demand of water per person would go down drastically, causes water stress [5,6]. Due to various anthropogenic reasons, the quality of water is decreasing every day and the polluted water harms aquatic systems, plants, and human beings. Several chemical components were reported in the water. Heavy metals in water are considered to be the most dangerous components and produce toxicity.

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The excretion of animals is also a major contributor to pollution in water [7–9].

Several water treatment techniques include, ion exchange process, reverse osmosis, flocculation, and filtration are used to remove the chemical components in the water. These technologies require higher energy, higher equipment, and maintenance cost [10]. The major drawback of using these conventional treatment techniques were disposal of the sludge which comes out after treating the wastewater. Therefore environmental eco-friendly removal of heavy metals is of growing significance. Several investigations have been made to utilize natural waste materials to remove toxic heavy metals by adsorption process [11]. Agricultural wastes that are unused and disposed in land can be utilized to remove contaminants in water. Some researchers utilized the agricultural wastes on the removal of heavy metals, and it has been previously reported [12–14]. The use of agricultural waste in developing countries in treating water was found to be effective. Residues of rice, dairy manure compost that is available in large quantities can be effectively used in removing heavy metal ions like zinc, copper, and lead. The maximum adsorption capacities for Zn(II), Cu(II), and Pb(II) were found to be 15.5, 27.2, and 95.3 mg/g, respectively, in the case of dairy manure compost [15,16]. The ability of biological materials to remove heavy metals through chemical means is known as biosorption. Bacteria, some parts of plants, and algae are known to be metal biosorbents [17].

In recent days, nanosized materials were used for wastewater treatment because of their exceptional performance. Due to its nano-size nature, it absorbs more particles resulting in high surface-to-volume ratio [18]. Nanosized materials are superior to other materials not only due to high surface to volume ratio and also shows high reactivity. The removal efficiency of heavy metal in water has been improved by the utilization of nanosized materials in treatment of water. Several clay minerals include kaolinite and montmorillonite were successfully used as an adsorbent [19]. The clay minerals have been superior in removing heavy metals like lead and arsenate. An increase in temperature improves the removal efficiency of heavy metal ions in the case of kaolinite clay [20].

The essential components included in the phase transfer process of adsorption techniques were adsorbate and adsorbent. A material that makes the ions to adhere on a surface is known as an adsorbent and the metal ions adsorb on the surface is adsorbate [21]. Adsorption technique is widely used nowadays to remove organic, inorganic, and biological toxic components. Among the other conventional methods, the adsorption technique is considered to be most effective because of its low maintenance cost, low operational cost, and easy handling nature [22]. The metal ions which are absorbed on the surface can be easily recovered using the adsorption technique. Several external factors include temperature, contact time, pH, adsorbent dozer, etc., affect the removal efficiency of toxic metal ions from the water [23]. Micro solid-phase extraction coating on the permeable membrane was originated in late 2006 as a substitute for solid-phase extraction. In the case of solid-phase extraction the adsorbent was packed in the permeable bag with heat arresting material. These residues

were used for the extraction of heavy metals from various samples. After adsorption of heavy metals, then it is desorbed with a suitable solvent and further investigated for the analysis of metals. Several other adsorbents were used to remove heavy metal ions include carbon nanoparticles [24], natural adsorbents [25], zeolites, etc. Over several adsorbents activated carbon gained significance because of its morphology, high surface area to volume ratio, adsorption efficiency, high cleaning capacity, and so on [26]. The disadvantage of using activated carbon for the removal of heavy metals is high cost and it is comparatively uneconomical than other adsorbents. Zeolites were considered as a good adsorbent material to remove hazardous metals in wastewater [27]. The objective of the study is to utilize avocado seed fibers in the removal of heavy metals from wastewater. The effect of seed powder on adsorption capacity based on pH, metal ion concentration, temperature, and contact time were assessed using batch technique [28]. Despite the many notable works, the removal of the metals from wastewater regarded to the avocado seeds were limited which is taken of interest in this work.

2. Materials and methods

Avocado seeds were collected in a local market, Chennai, Tamilnadu, and washed in a demonized water to remove the impurities in the surface of the raw materials. After washing with demonized water, the materials are allowed to dry in the open air for about 24 h and then dried the materials in the oven at 70°C for about 8 h. The oven-dried materials are then ground into a fine powder and then sieved through 100 micron sieve. Different heavy metal solutions were prepared which includes heavy metal ions of Pb(II), Cd(II), and Cu(II). The pH of the solution was found to be 5.8. The addition of 0.1 M NaOH and 0.1 M HCl solution adjusts the acidity level and pH of the heavy metal solutions.

2.1. Adsorption experiments

The adsorption experiments were carried out by mixing 100 g of powdered sample (avocado seed powder) with 100 mL of the heavy metal aqueous solution allowed to agitate in a water bath shaker at a constant speed of 250 rpm in a constant temperature and for a constant time interval. To avoid the uncertainties the testing were repeated a minimum 8 times for every cycle. After adsorption, the heavy metal solution was filtered and the concentration of heavy metal in aqueous solution after the filtration process was identified using atomic absorption spectrometry.

The adsorption quantity q (mg/g) of low-cost materials used in this study were to be identified using the following equation:

$$q = \frac{H_0 - H_e}{M} \times V \quad (1)$$

where H_0 (mg/L) and H_e (mg/L) are the initial and final concentration of toxic metals in the aqueous solution, respectively. V and M represent the volume of water used and the weight of the adsorbent used, respectively, in this study.

The percentage metal removal in the water can be found with the help of the following equation:

$$q(\%) = \frac{H_0 - H_e}{M} \times 100 \quad (2)$$

2.2. Crosslinking of seed powder

Crosslinking of seed powder was done in this study in order to increase the stability of the specimen in the solution. Crosslinking was achieved by immersing the seed powder in C_2H_5OH for about 10 min and then with calcium nitrate for 1 min at different time intervals. The seed powder is drained out from the solution and dried at a room temperature.

3. Results and discussion

3.1. Effect of cross-linking time

The seed powder used in this study was easily dissolved in water and it is necessary to enhance the metal absorption of seed powder in a liquid solution. To determine the impact of efficiency on the adsorption process with a crosslinking duration of Cd^{2+} , Pb^{2+} , and Cu^{2+} , crosslinking of avocado seed fibers in calcium solution at variable durations. The efficiency of adsorption on heavy metal ions using avocado seed fibers rises with rising duration of crosslinking and then remained constant beyond the crosslinking duration of 45 min. Thus, the optimum time of crosslinking used in this study was 45 min.

3.2. Fourier transform infrared characterization

Metal ion adsorption using avocado seed powder and possible bonds were characterized using Fourier transform infrared (FTIR) analysis. At the point when the seed powder are presented to IR radiation, comparing vibrational vitality of nuclear bonds is retained, and the FTIR spectra show absorbance power against the wave numbers

(or IR groups) relating to the respective frequencies at which certain groups/synthetic bonds in the specimen absorb IR.

Fig. 1 represents the FTIR a spectrum corresponds to $3,470\text{ cm}^{-1}$ represents the O–H stretching vibration. The spectra identified at $2,740\text{ cm}^{-1}$ corresponds to alkyl group of C–H vibration. The tremble mode of water was indicated at the $1,542\text{ cm}^{-1}$ of the spectra. The spectrum corresponds to peak $1,093\text{ cm}^{-1}$ represents C–N extending vibration. CH buckling vibration is represented by spectra on $1,299\text{ cm}^{-1}$. The occurrence of C–O–C extending vibrations and C–O extending vibrations of OH ions shown by the spectra at $1,073.23\text{ cm}^{-1}$.

Fig. 1 represents the FTIR spectra of after and before adsorption process of metal ions using avocado seed powder. The peak spectrum around $3,321$; $1,023$; and $1,134\text{ cm}^{-1}$ corresponds to hydroxyl ions, C–O and C–N synthetic bond in the metal ion adsorption.

3.3. SEM analysis

Fig. 2 represents the scanning electron microscopy images of before and after the adsorption process treated with avocado seed powder. After adsorption of Pb^{2+} , Cu^{2+} , and Cd^{2+} metal ions, the morphology has been changed and it is witnessed in SEM images. Fig. 2a represents the avocado seed powder cross-linked with ethanol consists of porous structure. Fig. 2b represents the adsorption of metal ions in avocado seed fibers and it represents the penetration of metal ions into the pore system thus ultimately improves the adsorption process. The voids in seed powder surface had been incredibly decreased after adsorption of metal ions which may have happened because of the bond arrangement with the groups present on the adsorbent. In view of the outcomes, it very well may be proposed that adsorbent morphology favors metal particle adsorption.

3.4. Effect of contact time

Based on previous researches the removal efficiency and adsorption property of a sample enhance with delayed

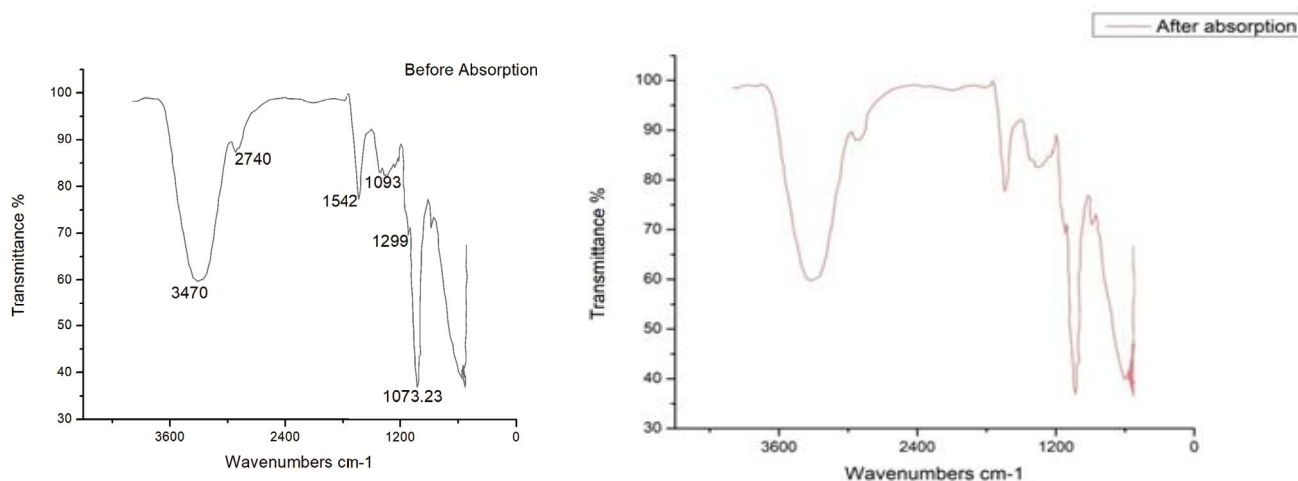


Fig. 1. FTIR spectra of after and before adsorption process of metal ions using avocado seed powder.

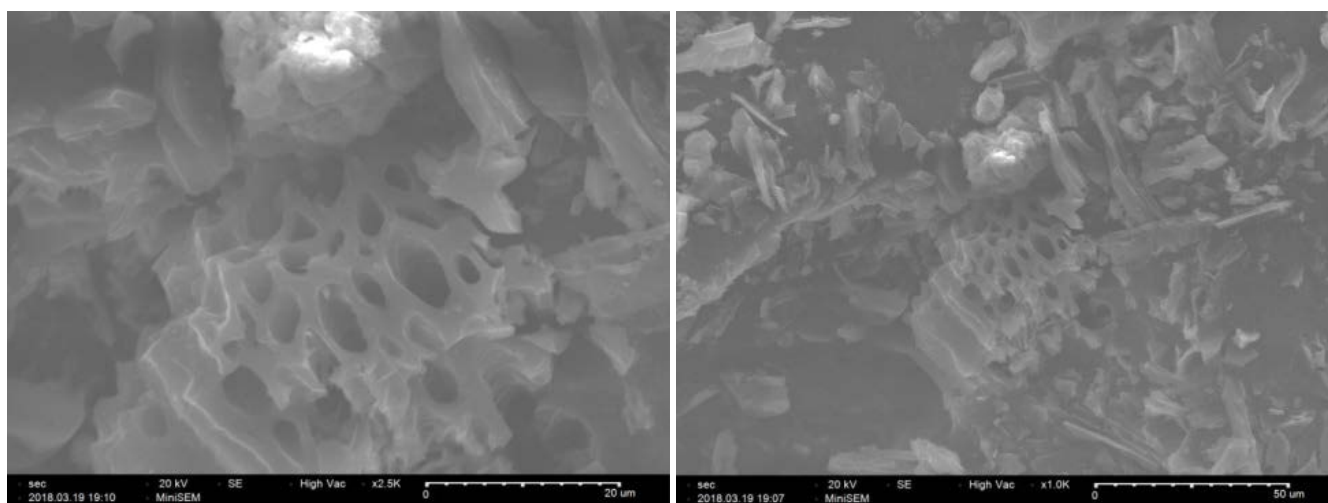


Fig. 2. SEM images of before and after the adsorption process treated with avocado seed powder.

contact time. The absorbent surface of the seed fibers were getting involved by the saturated adsorbate particles during the adsorption process. Beyond this saturation point, the efficiency of adsorption process does not gain any further increase, the adsorbents does not have ability to adsorb metal ions. Figs. 4–6 represents the impact on adsorption procedure based on the contact duration of adsorbents in water. Avocado seed fibers adsorbs Cd^{2+} , Cu^{2+} , and Pb^{2+} in faster manner, i.e., 95% of heavy metals adsorbed in a time duration of 15–20 min. Beyond the increment of 20 min had shown any notable change in the adsorption process using avocado seed fibers. The maximum adsorption was achieved at 40 min to adsorb Cd^{2+} , Cu^{2+} , and Pb^{2+} heavy metals at an efficiency of 98.23%, 99.12%, and 99.29%, respectively.

3.5. Effect of solution acidity

In order to identify the impact of heavy metal adsorption on an acid solution, 100 mg of crosslinked avocado seed powder were blended in with 100 mL of 1.5 mM $\text{Cu}^{2+}/\text{Pb}^{2+}/\text{Cd}^{2+}$ arrangement for a duration of 30 min at various pH ranges. From Fig. 3, it is evident that at a very low pH range the efficiency of the adsorption process is very minimal which indicated the adsorption destinations were reacted with hydrogen atoms. The unsaturated portion of avocado seed strands attracts the hydrogen atoms and heavy metals present in the solution [29]. The efficiency of adsorption of heavy metals are high as pH increases. In Fig. 3, the pH ranges between 4 and 7, achieved maximum adsorption, and beyond this pH range there is no significant improvement in adsorption process.

3.6. Effect of contact time and environmental temperature

From Figs. 4–6 the adsorption limit of avocado seed fibers for removal of heavy metals increases with rise in contact duration and beyond the certain limit there is no improvement in adsorption when contact time increases. The rate of adsorption is very fast during the first 30 min

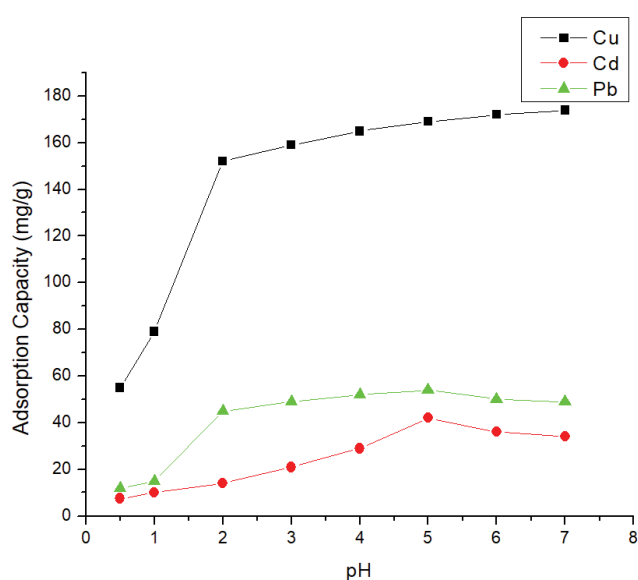


Fig. 3. Effect of pH on adsorption capacity of heavy metals.

due to favorable structure of avocado seed fibers. The permeable nature of the fibers enables the adsorption of heavy metals efficiently and gives an ideal pathway for avocado seed powder to adsorb heavy metal ions [30,31]. Pseudo-first and pseudo-second-request dynamic models enable to understand the behavior of the adsorption process with respect to contact duration.

Fig. 7 depicts the adsorption capacity of avocado seed fibers on heavy metal ions with respect to temperature. The adsorption capacity of avocado seed powder increases marginally with rise in temperature. In all the cases, the degree of adsorption is not exceptional due to ideal pathway of ions given by the seed fibers, making the adsorption process less dependent on temperature variation [32,33]. The powerless affectability of avocado seed powder on adsorption process with respect to temperature is pivotal to down to earth applications.

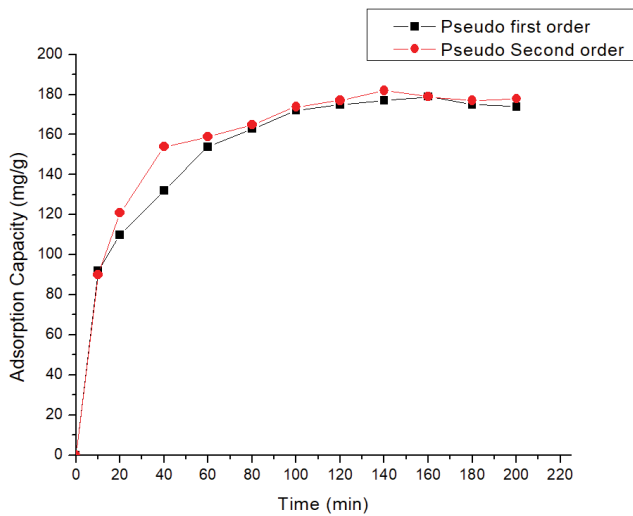


Fig. 4. Adsorption kinetics of Cu^{2+} ions on avocado seed powder.

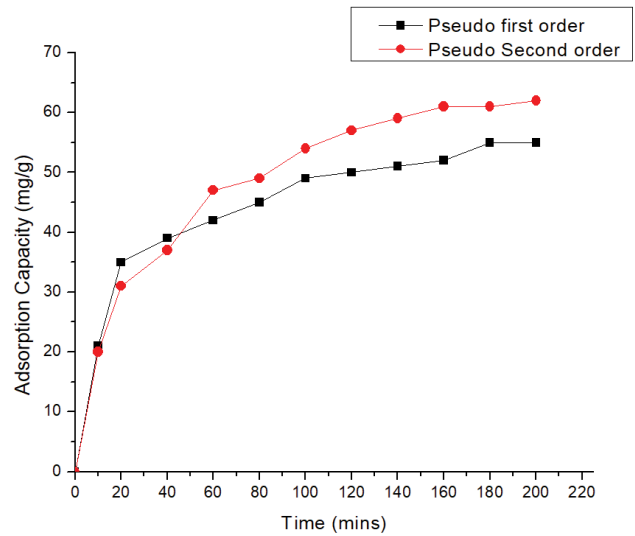


Fig. 6. Adsorption kinetics of Cd^{2+} ions on avocado seed powder.

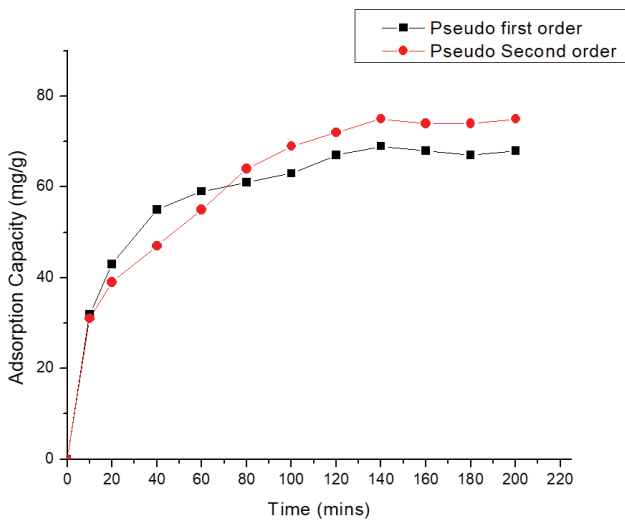


Fig. 5. Adsorption kinetics of Pb^{2+} ions on avocado seed powder.

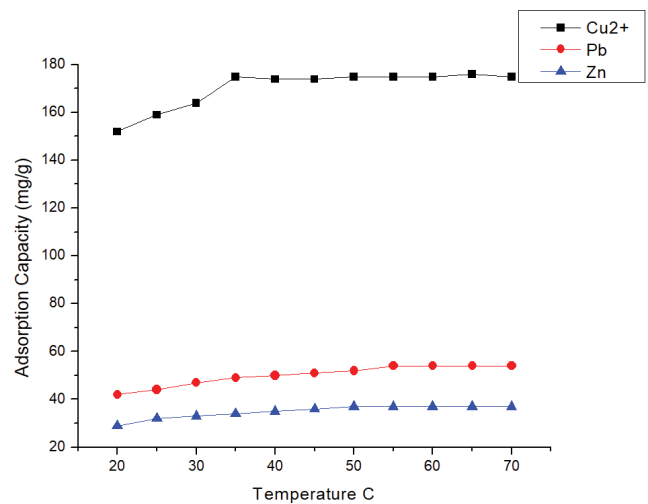


Fig. 7. Adsorption capacity of avocado seed powder with respect to temperature.

3.7. Maximum adsorption capacity and selectivity

The quantity of adsorbent used in solution to remove heavy metals is entirely based maximum adsorption capacity of adsorbent. Fig. 8 depicts the adsorption capacity of avocado seed fibers with respect to varying concentration levels of heavy metal ions. The adsorption capacity of heavy metal increases as the concentration levels of heavy metals in solution increases and beyond the certain limit it stayed constant, indicates there is no dynamic pathways available in the seed fibers to adsorb the heavy metals and yield the saturation limit of process [34]. The most extreme adsorption limits of avocado seed fibers for Cu^{2+} , Pb^{2+} , and Cd^{2+} in this investigation were 179.7, 52, and 38.65 mg/g, respectively.

Furthermore, serious adsorption tests ($\text{Pb}^{2+}/\text{Cu}^{2+}$, $\text{Pb}^{2+}/\text{Cd}^{2+}$, and $\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Cd}^{2+}$) were directed to assess the selectivity of avocado seed powder. From Fig. 9, the avocado seed strands can take-up 78.1% of Cu^{2+} , 32.5% of Pb^{2+} ,

and 24.2% of Zn^{2+} from unadulterated Pb^{2+} , Cu^{2+} , and Zn^{2+} arrangements, individually. Be that as it may, when harmony with blended $\text{Pb}^{2+}/\text{Cu}^{2+}$ arrangement, 76.5% of Pb^{2+} , and just 22.5% of Cu^{2+} were retained is shown in Fig. 9. Comparative outcomes were additionally seen in $\text{Pb}^{2+}/\text{Cd}^{2+}$ and $\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Cd}^{2+}$ arrangement.

4. Conclusion

In this study, avocado seeds available in the local market were collected, processed, and powdered in to fiber strands. The seed fibers were tested for adsorption capacity of heavy metals in wastewater. Initially, the surface morphology of seed fibers looks porous in nature and after subjected to treatment, the permeable nature of the seed powder surface had been incredibly decreased

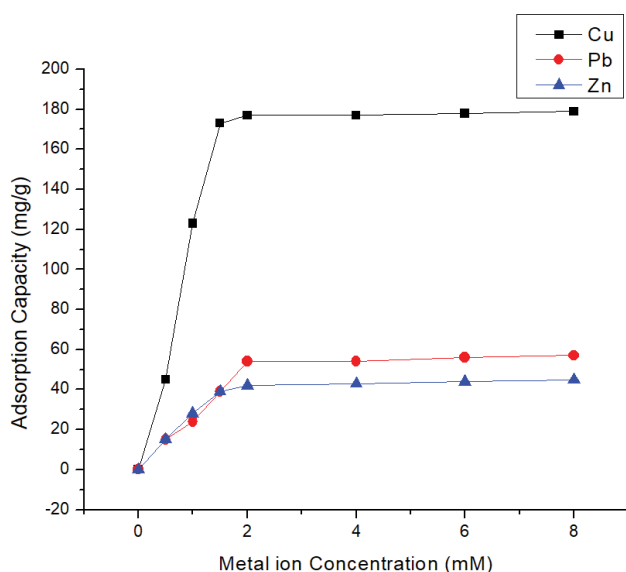


Fig. 8. Adsorption capacity based on metal ion concentration.

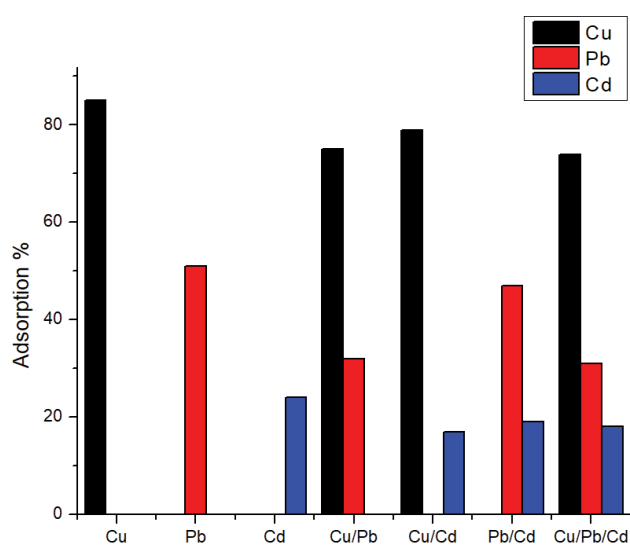


Fig. 9. Heavy metal removal efficiency with and without other metals.

after adsorption of metal ions which may have happened because of the bond arrangement with the groups present on the adsorbent. In view of the outcomes, it very well may be proposed that adsorbent morphology favors metal particle adsorption. The optimum contact time on adsorption of heavy metals was found to be 40 min. The adsorption capacity of seed fibers had not depended on temperature. The maximum adsorption capacity of Cd^{2+} , Cu^{2+} , and Pb^{2+} were found to be 61.4, 178.21, and 79.3 mg/g, respectively. Sustainable economical material, less temperature dependant properties of avocado seed fibers make an ideal material for wastewater treatment.

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